HOT-WATER UPGRADING OF LOW-GRADE COAL: FUNDAMENTALS AND SLURRY RHEOLOGY

M. Rashid Khan and Todd Potas[+]
Texaco Research & Development,
P.O. Box 509, Beacon, NY 12508

[+]The University of North Dakota, Energy & Environmental Research Center, Grand Forks, ND 58202

ABSTRACT

Extensive bench-scale and pilot-plant studies have been conducted to better understand the fundamentals of hot-water drying of coal and the rheology of treated coal-water slurry. There was an increase in the heating value of the hot-water dried coal via decarboxylation. The formation of tar and extractables reduces the surface area and accessibility of water into the coal structure. As a result of decarboxylation and tar formation, the treated coal becomes relatively more hydrophobic. The slurry prepared from the hot-water dried coal was highly stable towards settling. The moisture reabsorption for the hot-water dried coal was minimal. Finally, the energy density of the slurry prepared from the hot-water dried coal approached those prepared from bituminous coals.

INTRODUCTION & BACKGROUND

The use of coal via gasification offers an excellent avenue to generate electric power with an increased efficiency for both energy recovery from coal as well as removal of pollutants (i.e., sulfur and nitrogen containing species). High-temperature pressurized, entrained-flow gasifiers (such as those used in The Texaco Coal Gasification Process) offer attractive options for integrated gasification combined cycle applications due to their high-throughput and low-level of contaminant production.

In many coal utilization processes, coal-water slurry fuel is used (1-5). Transport of coal into the gasifier by slurrying it with water offers several advantages: (a) the pumping technologies are proven and reliable, valves and flow measurement devices can be used; (b) the slurry feed is homogeneous, predictable and safe; (c) the presence of water in the slurry acts as a temperature moderator; resulting in reduced thermal wear. The high inherent moisture of low-rank coal (LRC), however, prevents the formation of coal slurry with high solids content needed for efficient operation. This necessatitates a method for preparing a slurry that is pumpable and still contains high energy density (i.e., solids content) to permit gasification at a reasonable rate of oxygen consumption. This implies the need to irreversibly reduce the moisture content of the coal.

Hot-water drying (also known as "hydrothermal treatment" or "wet carbonization") of coal, initiated several decades ago (6-9), offers an excellent avenue to efficiently achieve the objectives of a suitable slurry for gasification. The aim of this study is to review the fundamental aspects of hot-water drying of low-rank coals.

EXPERIMENTAL

Hot-water drying of coal was conducted in various reactors: batch autoclave reactors, and a continuous thermal treatment reactor. One of the batch reactors consists of a 3.8 liter electrically heated autoclave and numerous thermocouples and pressure transducers. The unit was designed so that the reactant materials could be charged rapidly into a preheated autoclave from a piston-type accumulator. This allowed the charge materials to reach operating temperature in the relatively short time of 5 to 10 minutes. It also allowed for close control of residence times as the entire contents of the autoclave reactor charged into a 7.6 liter quench vessel at room temperature to end the drying and pyrolysis reactions rapidly. After quenching, the evolved gases were vented through cold traps (and were metered and analyzed). Description of the continuous thermal treatment reactor is presented elsewhere (4,5).

RESULTS & DISCUSSION

Influence of Pretreatment Temperature/Residence Time: For a given viscosity, the dry-solids content increased with the increasing processing temperature. The viscosity versus solids contents for slurries made from treated (at various temperatures) Indian Head Lignite is shown in Figure 1. At a viscosity of 800 cP, the

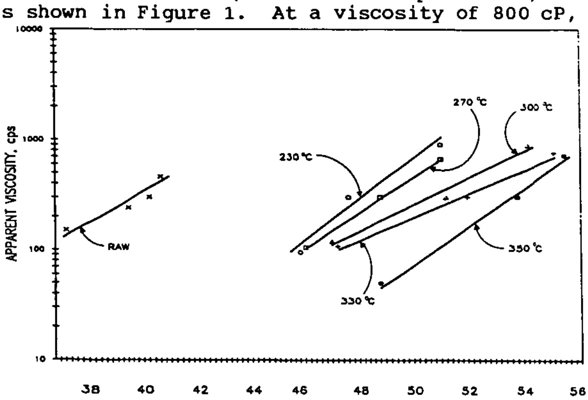

Figure 1. Apparent viscosity at 410 s^{-1} and 28°C versus solids content for coal/water slurry prepared from Indian Head Lignite before and after hydrothermal treatment

solids content increased from 42.5% to 55.5% (at a shear rate of 410 sec^{-1} at 28 °C) after processing at 350°C. In addition, the higher the pretreatment temperature, the higher the solids contents, for a given viscosity of 800 cP. The slurry energy content also increased by pretreatment at 330°C (1,4).

As a result of pretreatment at 330°C, the slurry prepared from Indian Head lignite contained 150 percent of the heat content of the raw slurry. An increase in pretreatment temperature resulted in an increase in heating values for all coals (Figure 2), although to a lesser extent for higher rank coals. The influence of residence time of pretreatment on the slurry solids content is shown in Figure 3. The longer the residence, the greater the slurryability of the products. An increase in pretreatment temperature also reduced the equilibrium moisture content for all coals (Figure 4), measured soon after pretreatment.

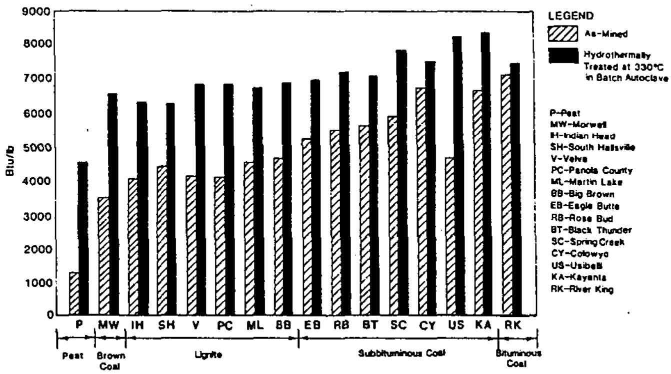

Figure 2. Slurry heating value (dry-basis) of raw and 330°C treated coal at maximum solids concentration.

<u>Influence of Coal Type</u>: The lower the rank of the coal, the greater the reductions in equilibrium moisture content (Figure 4) upon pretreatment. This effect is attributable to the higher concentrations of oxygen functional groups and the associated water molecules present in the lower rank coals.

The changes to the coal structure as a result of hydrothermal treatment were irreversible, and the coal maintained a low equilibrium moisture content in either air or water, unlike the untreated coal.

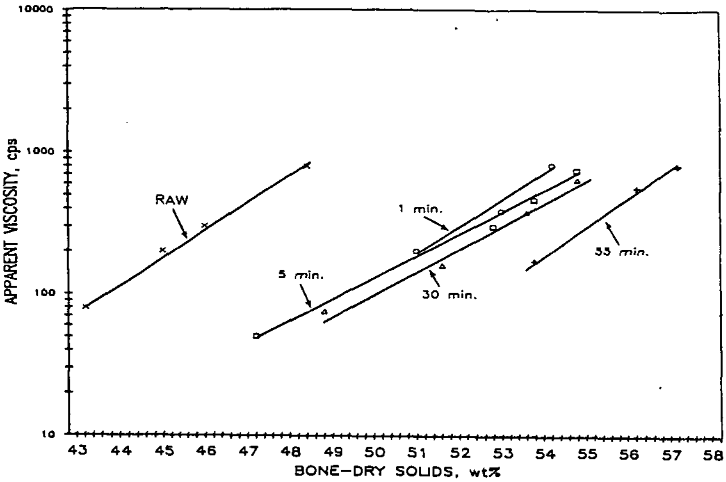

Figure 3. Apparent viscosity versus solids content for a subbituminous coal (Spring Creek, Montana) processed at 330°C at various residence times in a continuous reactor.

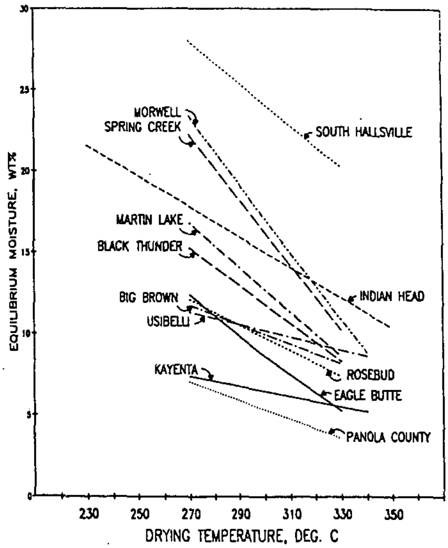

Figure 4. Equilibrium moisture versus pretreatment (hot-water-drying) temperature of various coals.

CP/MAS: Cross Polarization/Magic Angle Spinning (CP/MAS) Solid State C^{13}-NMR spectroscopy provided interesting results on the effects of hot-water drying on the structure of the processed coal. Spectra for as-received and the hydrothermally treated coals (at 330°C, Indian Head lignite) are shown in Figure 5. The raw lignite contained large quantities of aliphatic material, long chain waxes and alkanes. However, when the coal was hydrothermally treated at 330°C there was a dramatic reduction in these groups, perhaps as a result of cracking and extraction. Many coals examined exhibited a significant weight-loss due to expulsion of carboxylic groups during thermal treatment. The carboxylic groups, unlike aliphatic compounds, do not contribute significantly to the heating value of coal. Thus, the loss of these oxygenated functional groups actually enhances the energy density of the product.

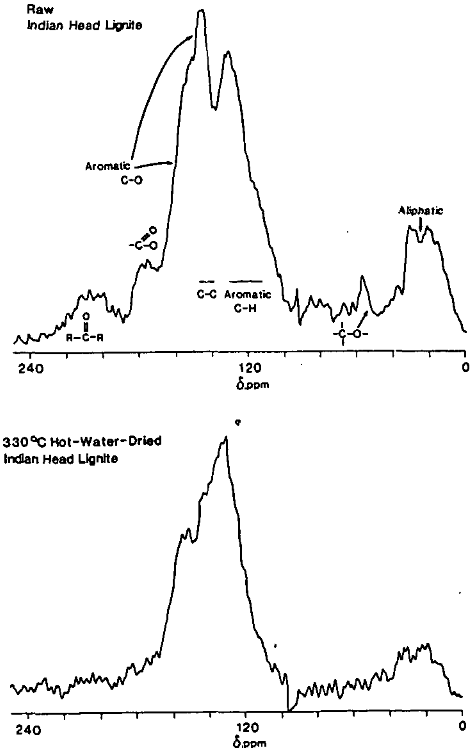

Figure 5. Solid-state ^{13}C NMR spectra for as-mined and 330°C hot-water dried Indian Head (North Dakota) lignite.

Evolved Products: Table 1 provides additional data on the influence of pretreatment temperature on coal structure, and on the nature of the evolved products as a result of heat-treatment. After hydrothermal treatment of Indian Head Lignite at 340°C, the yield of phenolics, alcohols and hydrocarbon gases represented less than 1 wt% of the raw maf coal, while the yield of decarboxylation products (CO_2, CO and H_2O) represented nearly 18% of the products. Decarboxylation of coal had a major effect on reducing the hydrophilic nature of coal, as reflected by the decreases in the equilibrium moisture content.

Formation of Extractables: A significant impact of hydrothermal-treatment was also reflected in the exuded tar yield from the treated coal. The yield of extractables (tar) was significantly increased as a result of hydrothermal treatment (Figure 6). The

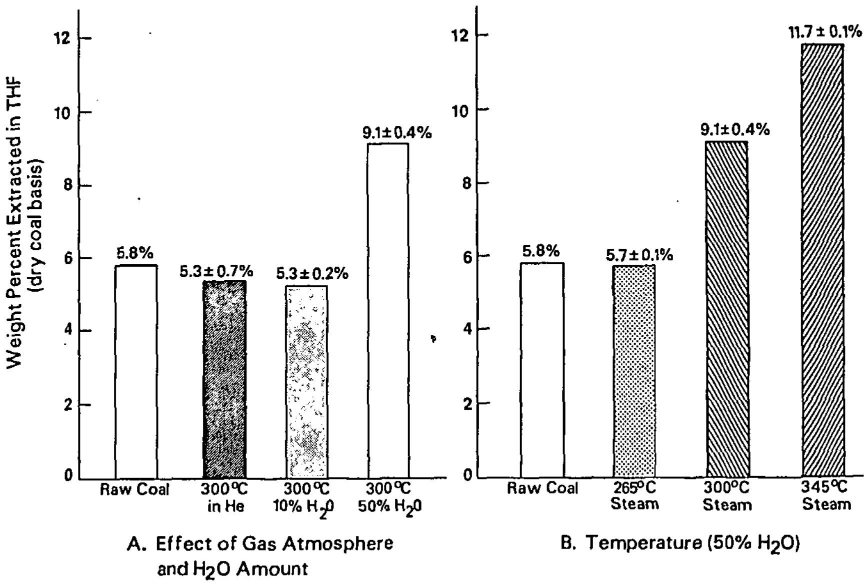

Figure 6. Effect of hot-water-drying of coal on extractable yield

Table 1

COMPARISON OF MATERIAL BALANCE RESULTS FOR HYDROTHERMALLY TREATING INDIAN HEAD LIGNITE IN A COLD-CHARGE AUTOCLAVE

Coal	Indian Head				
Process Temp., °C	231	272	302	333	348
Process Pressure, Psig	400	900	1,400	2,300	2,500
Net Yields - wt% maf coal[a]					
Decarboxylation and Dehydration Products ($CO+CO_2+H_2O$)	1.6	9.8	13.8	14.8	17.5
Pyrolysis Product Gases ($H_2+C_1-C_4+H_2S+NH_3$)	0.0	0.0	0.2	0.2	0.1
Pyrolysis Product Liquids (Phenols, Methanol, Acetone, MEK)	0.0	0.2	0.4	0.4	0.8
Residual maf coal	98.1	92.2	87.7	85.9	83.1
Energy Recovery, %	100.0	98.2	97.8	98.4	96.6
Product Coal Characteristics					
Heating value, mf basis, Btu/lb	10,400	10,800	11,200	11,400	11,600
Equilibrium Moisture, wt %	20.9	18.0	14.5	13.5	7.4
lbs ash/MM Btu	14.83	13.28	13.44	13.93	14.02
lbs sodium/MM Btu	0.53	0.47	0.42	0.42	0.27
lbs sulfur/MM Btu	1.03	0.98	1.00	1.02	0.94
Coal-Water Slurry Properties[b]					
Maximum measured solids concentration, wt%	51.0	50.9	54.2	55.3	55.6
Apparent viscosity, cps					
at 100 sec^{-1} and 28°C	1,770	1,530	1,280	1,420	1,190
at 410 sec^{-1} and 28°C	890	650	860	740	710
Heating value, Btu/lb	5,300	5,500	6,070	6,300	6,450

[a]Net yields do not total 100% because of errors introduced by the changing inorganic content of the coal and the changing ways it behaves when samples are ashed.

[b]The data shown is for samples which were first filtered without washing and then reslurried in deionized water. For some coals significant improvements were seen when the filter cake was washed.

yield of tar was quantified by extracting the treated coal with tetrahydrofuran (THF), as described elsewhere (3). For the Illinois No. 6, the yield of extractables increased significantly with the increase in pretreatment temperature. The influences of gas atmosphere (amount of water) and temperature of pretreatment are shown in Figure 6.

Surface Area of Treated Products Compared to Feed: An important change involved the sealing of the coal pores which exuded the tar. The influence of tar condensation on coal pores (and openings) and surfaces resulted in a decrease in the surface area (i.e., accessibility) as well as the hydrophilic nature of coal. As a result, the surface area of the hot-water dried coal decreased by 30 to 40%, as determined by BET (Brunauer, Emmett, and Teller) approach.

REFERENCES:

1. Potas, T. et.al "Preparation of Hydrothermally Treated LRC-Water Slurries", Chem. Engr. Comm., Vol. 44, pp 133-151, 1986.

2. Khan, M. R., W. Chem. and E. Suuberg, "Influence of Steam Pretreatment on Coal Composition and Devolatilization," Energy & Fuels 3, March/April, 1989.

3. Khan, M. R., "An Overview of Mild Gasification Research," Proceedings, Gasification Contractors' Meeting, US Dept. of Energy, June 27-29, 1989.

4. Willson, W. G. et. al, "Low-Rank Coal Water Slurries for Gasification," Final Report by UNDEERC, EPRI Report No. AP-4262, Nov., 1985.

5. Potas, T. A. et. al, "Pilot Scale Preparation of Lignite and Sub-bituminous Coal Water Fuels," Coal/Water Slurry Preparation and Utilization Conference, Orlando, FL, May 1985

6. H. Klein, "The Fleissner Method of Drying Lignites; Its Underlying Chemical and Physical Principles", BRAUN Kohle 29, 1-30, 1930.

7. G. A. Wiltsee, "Low-Rank Coal Research" Quarterly Report July-September, 1984. University of North Dakota Energy Research Center. Technical Report DOE/FE/60181-1682. Technical Information Center. U.S. Department of Energy.

8. H. Fleissner, U.S. Patent 1,632,829, 1927; H. Fleissner, U.S. Patent 1,679,078, 1928.

9. B. Stanmore, D. N. Baria and L. E. Paulson, "Steam Drying of Lignite: A Review of Processes and Performance", DOE/GFETC/RI-82/1, (DOE 82007849), 1982.